

## PATENT SPECIFICATION

NO DRAWINGS

928.704



Date of Application and filing Complete Specification: Dec. 1, 1961.

No. 43152/61.

Application made in Germany (No. F32680 Ivb/I2o) on Dec. 2, 1960.

Complete Specification Published: June 12, 1963.

BEST AVAILABLE COPY

Index at acceptance:—Classes 2(3), C1E4K(2:7), CP(1L1:3C:7); and 81(1), E1C3B1, E1C4A(2:3:4).

International Classification:—C07c, f. (A01n).

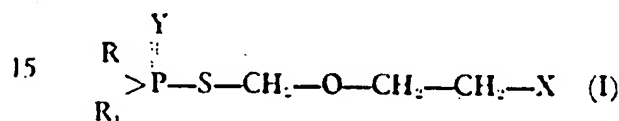
## COMPLETE SPECIFICATION

## Phosphoric, Phosphonic and Phosphinic Acid Esters and the Thio Analogues thereof

We, FARBENFABRIKEN BAYER AKTIEN-GESELLSCHAFT, a body corporate organised under the laws of Germany, of 22c, Leverkusen-Bayerwerk, Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention is concerned with new and useful insecticidal compounds and with a new process for their production.

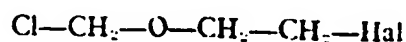
The new compounds according to the present invention may be represented by the general formula:—



wherein X stands for a chlorine or bromine atom or for an alkylmercapto radical containing 1 to 4 carbon atoms or for a phenylmercapto or benzylmercapto radical, Y is an oxygen or sulphur atom and R and R<sub>1</sub>, which may be the same or different, are alkyl, alkoxy or alkylmercapto radicals containing 1—4 carbon atoms, with the proviso that when X is an alkylmercapto radical, R and R<sub>1</sub> cannot both be alkoxy radicals.

Compounds are known which are made by esterifying  $\alpha$ -chloromethyl ethers or -thioethers (which are readily obtainable from alcohols or mercaptans, formaldehyde and hydrochloric acid) with dialkyl-dithiophosphoric acids.

We have found that there may readily be obtained from ethylene - halohydrins, formaldehyde and hydrochloric acid the  $\beta$ -haloethyl chloromethyl ether of the following composition:—



wherein Hal is a chlorine or bromine atom, [Price 4s. 6d.]

and we have also found that this  $\beta$ -haloethyl-chloromethyl ether readily reacts with mono-thio- or dithio-phosphoric, -phosphonic or -phosphinic acids in such a manner that compounds of general formula (I) are formed, in which X stands for a chlorine or bromine atom.

We have also found that the halogen in the aforesaid compounds may easily be exchanged for a mercaptan radical, even at low temperatures, by reaction with a mercaptan of the general formula R'SH, in which R' is an alkyl radical containing 1—4 carbon atoms, a phenyl radical or a benzyl radical, compounds of the general formula (I) thus being formed, in which X stands for the above-defined mercaptan radical.

The exchange of halogen for the mercaptan radical is advantageously carried out in the presence of an acid-binding agent. Sodium alcoholates have proved to be especially suitable for this purpose. The exchange of halogen for the mercaptan radicals is also preferably effected in an inert solvent. Preferred inert solvents are benzene, toluene and anhydrous diethyl ether.

Some dithiophosphoric acid esters similar to those of the above general formula (I) are already known from Acta chimica sinica, 25, 408/1959. According to this publication, these esters are obtained by condensation of dithiophosphoric acids, mercaptans or alcohols and aldehydes; however, by this method of operation, the compounds are obtained, if at all, in a very small yield and in a state of very great impurity, whereas by the stepwise method of production according to the present invention, the compounds are obtainable in a very good yield and in great purity.

The new compounds according to the present invention are distinguished by their markedly systemic action, in addition to generally good insecticidal properties. They very effectively kill insects, such as flies, mites and aphids. They distinguish themselves

40

45

50

55

60

65

70

75

80

20. Esters of the general formula given in claim 16, whenever prepared by the process according to any of claims 19 to 22.

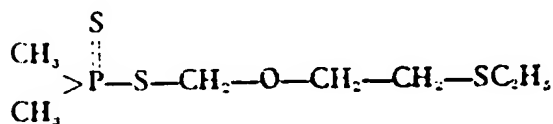
- 5 21. Insecticidal compositions containing an ester of the general formula given in claim 1 and a solid or liquid diluent or extender.

For the Applicants,  
CARPMAELS & RANSFORD,  
Chartered Patent Agents,  
24, Southampton Buildings,  
Chancery Lane, London, W.C.2.

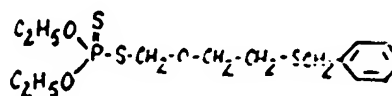
Leamington Spa: Printed for Her Majesty's Stationery Office, by the Courier Press (Leamington) Ltd.—1963. Published by The Patent Office, 25 Southampton Buildings, London, W.C.2, from which copies may be obtained.

BEST AVAILABLE COPY

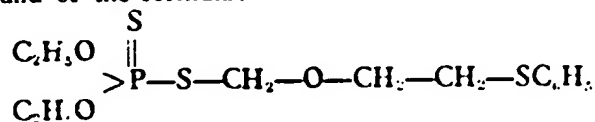
7. The compound of the formula:—



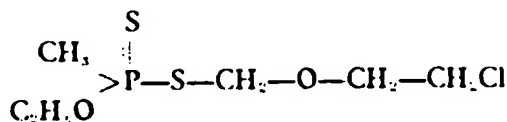
8. The compound of the formula:—



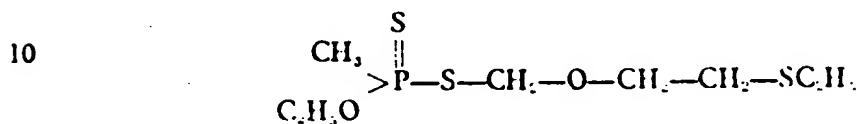
9. The compound of the formula:—



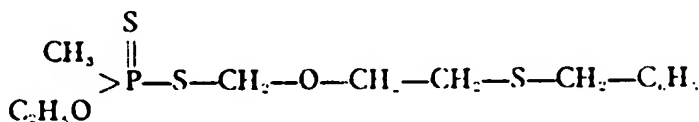
10. The compound of the formula:—



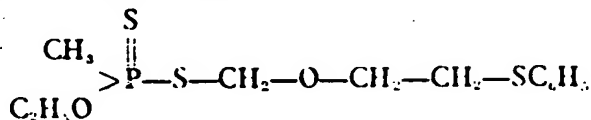
11. The compound of the formula:—



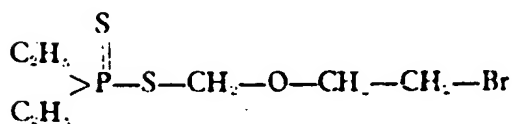
12. The compound of the formula:—



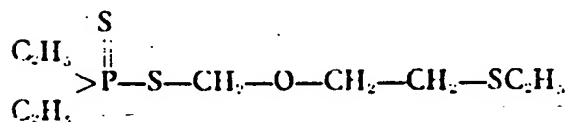
13. The compound of the formula:—



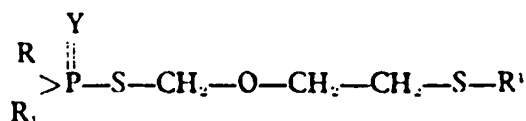
14. The compound of the formula:—

1—4 carbon atoms or a phenyl or benzyl radical, which comprises reacting a  $\beta$ -haloethyl chloromethyl ether of the general formula

15. The compound of the formula:—



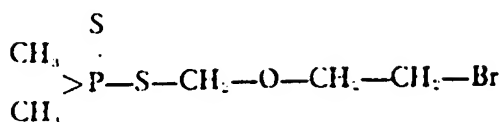
16. The process for the production of esters of the formula:—

in which R, R<sub>1</sub> and Y have the same meanings as above and R<sup>1</sup> is an alkyl radical containingin which Hal is a chlorine or bromine atom, with a monothio- or dithio-phosphoric, -phosphonic or -phosphinic acid and then reacting the resultant  $\beta$ -haloethyl ester with a mercaptan of the general formula R<sup>1</sup>—SH, in which R<sup>1</sup> has the same meaning as above.

17. Process according to claim 16, wherein the reaction with the mercaptan is carried out in the presence of an acid-binding agent.

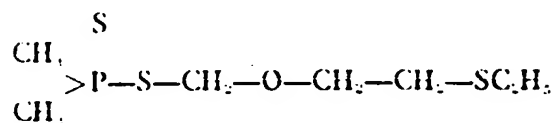
18. Process according to claim 16 or 17, wherein the reaction with the mercaptan is carried out in the presence of an inert solvent.

19. Process according to claim 16 for the production of esters of the general formula given therein, substantially as hereinbefore described and with reference to any of the specific Examples.



are obtained. Yield 75% of the theoretical.

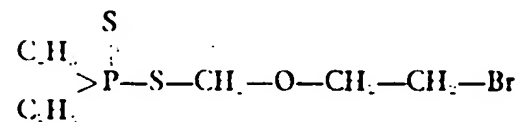
- 5 16 grams (0.25 mol) ethyl-mercaptan are dissolved in 150 cc. benzene, with the addition of a sodium ethylate solution containing 0.25 mol of sodium. 66 grams (0.25 mol) of the above  $\beta$ -bromoethyl ester are added at 15–20° C. to this solution. Stirring is continued for one hour at 20° C. and the reaction product then taken up in 200 cc. benzene. It is washed neutral with water, the benzene solution then dried with anhydrous sodium sulphate and fractionated. In this way, 32 grams of the new ester of the following formula:



and of b.p. 87° C./0.01 mm Hg are obtained. Yield 53% of the theoretical.

#### EXAMPLE 5.

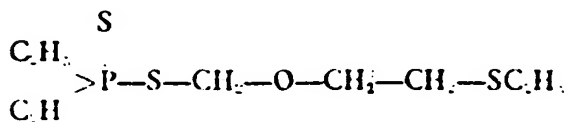
- 20 154 grams (1 mol) diethyl-thionothiophosphinic acid are dissolved in 100 cc. benzene. 174 grams (1 mol)  $\beta$ -bromoethyl- $\gamma$ -chloromethyl ether are added at 50° C., with stirring. After warming the mixture for one hour, the formation of hydrochloric acid has ceased. The reaction product is taken up in 200 cc. benzene, washed neutral with water and dried with anhydrous sodium sulphate. After distilling off the solvent, 215 grams  $\beta$ -bromoethyl ester of the formula:



are obtained. Yield 74% of the theoretical.

73 grams (0.25 mol) of the above  $\beta$ -bromoethyl ester are added dropwise at 20° C., with

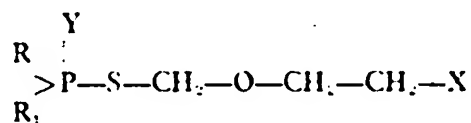
stirring, to a solution of 16 grams (0.25 mol) ethyl-mercaptan in 150 cc. benzene and a sodium ethylate solution containing 0.25 mol sodium; stirring is continued at 20° C. for one hour and the reaction product then diluted with 300 cc. benzene, washed neutral with water and dried with anhydrous sodium sulphate. Upon fractionation, 45 grams of the new ester of the formula:



and of b.p. 106° C./0.01 mm Hg are obtained. Yield 66% of the theoretical.

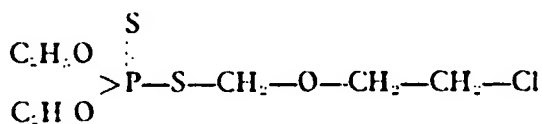
WHAT WE CLAIM IS:—

1. Esters of the general formula:—

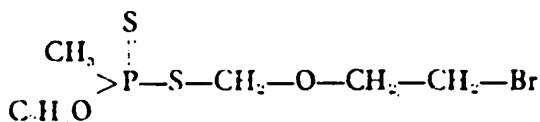


wherein X stands for a chlorine or bromine atom or for an alkyl mercapto radical containing 1 to 4 carbon atoms for a phenyl-mercapto or benzylmercapto radical, Y stands for an oxygen or sulphur atom and R and R<sub>1</sub>, which may be the same or different, stand for alkyl, alkoxy or alkyl-mercapto radicals containing 1–4 carbon atoms, with the proviso that when X is an alkylmercapto radical, R and R<sub>1</sub> cannot both be alkoxy radicals.

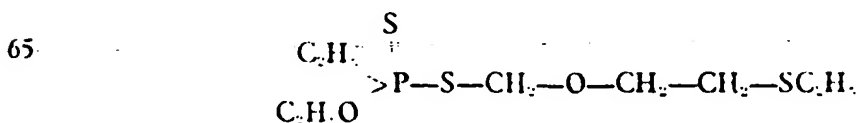
2. The compound of the formula:—



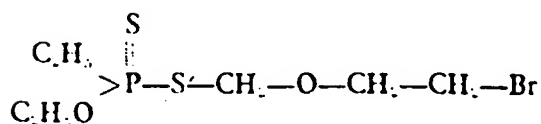
3. The compound of the formula:—



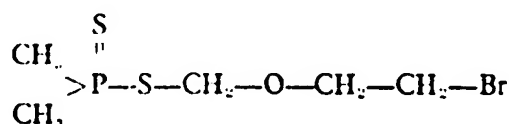
4. The compound of the formula:—



5. The compound of the formula:—



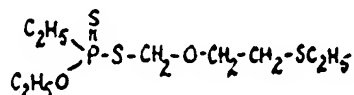
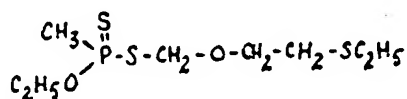
6. The compound of the formula:—



especially by a good contact-insecticidal activity and, at the same time, by an activity on eating insects, such as caterpillars. The compounds may be used in the same manner as other known phosphoric acid insecticides, i.e. in a concentration from about 0.00001 to about 1% by weight, diluted or extended with suitable solid or liquid carriers or diluents. Examples of such solid carriers are talc, chalk, bentonite and clay and as liquid carriers there may be mentioned water (if necessary with commercial emulsifiers), alcohols, especially methanol or ethanol, ketones, especially acetone or methyl ethyl ketone, and liquid hydrocarbons. The new compounds may also be used in combination with each other or with for example, known insecticides and/or fertilisers.

As examples of the special utility of the new compounds, the esters of the following formulae:

I)

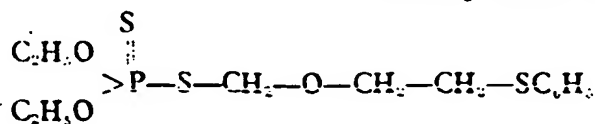


II)

were tested against flies and caterpillars, respectively. Aqueous solutions of the aforementioned compounds were prepared by admixing them with the same amount of an auxiliary solvent (acetone). A commercial emulsifier (benzyl hydroxy diphenyl polyglycol ether) was added in an amount of 20%, referred to active ingredient. This premixture was then diluted with water to the desired concentration. The tests were carried out as follows:

(a) against flies (*Musca domestica*). About 50 flies were placed under covered petri dishes in which drip wet filter papers had been placed which had been sprayed with an insecticidal solution of a concentration as shown below. The living status of the flies was determined after 24 hours. The following result was obtained:

Compound	aqueous concentration (in % active ingredient/water)	killing rate (in %)
I)	0.001	100



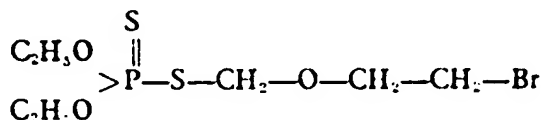
(b) against caterpillars: white cabbage were sprayed drip wet with aqueous emulsions prepared as above in a concentration as indicated below. Caterpillars (of the type diamond black moth, 10 each) were placed on the sprayed leaves of the white cabbage. The living status was determined after 24 hours and 48 hours. The following result was obtained:—

Compound	aqueous concentration (in % active ingredient/water)	killing rate (in %)
II)	0.1	100

The following Examples are given for the purpose of illustrating the present invention:—

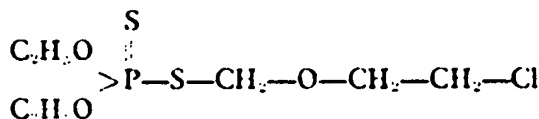
#### EXAMPLE 1.

186 grams (1 mol) O,O - diethyl - dithiophosphoric acid are placed in a flask equipped with an agitator. 174 grams (1 mol) β-bromoethyl - α - chloromethyl ether (b.p. 38° C./2 mm Hg) are added with stirring. Stirring is continued at 60° C. for one hour. The bulk of the hydrochloric acid formed in the reaction is then split off. The reaction product is taken up in 300 cc. benzene and washed neutral with water. The reaction product is subsequently dried with anhydrous sodium sulphate and fractionated. 220 grams of the ester of the following formula:

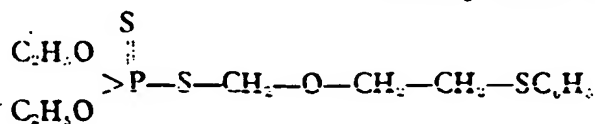


and of b.p. 88° C./0.01 mm Hg are obtained. Yield 68% of the theoretical.

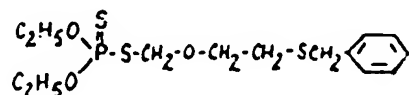
In the same way, the compound of the following formula may be obtained:



27.5 grams (0.25 mol) phenyl - mercaptan are dissolved in 100 cc. benzene with the addition of a sodium ethylate solution containing 0.25 mol sodium. 81 grams (0.25 mol) of the bromine-containing ester obtained as described above are added dropwise at 20° C., with stirring. Stirring is continued for one hour and the reaction product then taken up in 300 cc. benzene. The benzene solution is washed neutral with water and then dried with anhydrous sodium sulphate. Upon fractionation, there is obtained the product having the following constitution:—

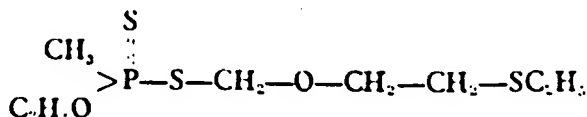


In the same way, the compound of the following formula may be obtained: —



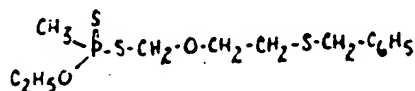
#### EXAMPLE 2.

- 5 156 grams (1 mol) methyl-thionophosphonic-O-ethyl ester thiolic acid (b.p. 32° C./0.05 mm Hg) are dissolved in 100 cc. benzene. 174 grams (1 mol)  $\beta$ -bromoethyl- $\alpha$ -chloromethyl ether are added at 50° C., with stirring. Stirring is continued for one hour at 50° C. The evolution of hydrochloric acid has then ceased. The reaction product is taken up in 300 cc. benzene. The benzene solution is washed neutral with water, dried with anhydrous sodium sulphate and subsequently fractionated. In this way, 172 grams of the new ester of b.p. 80° C./0.01 mm Hg are obtained. Yield 59% of the theoretical.

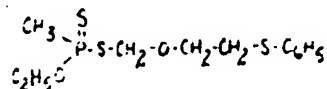


- 35 of b.p. 96° C./0.01 mm Hg are obtained. Yield 67% of the theoretical.

In the same way, the compounds of the following formulae may be obtained:

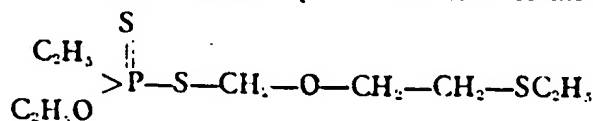


40



#### EXAMPLE 3.

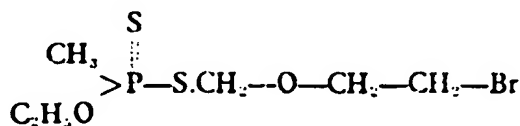
- 45 170 grams (1 mol) ethyl-thionophosphonic-O-ethyl ester thiolic acid (b.p. 38° C./0.01 mm Hg) are dissolved in 100 cc. benzene. 174 grams (1 mol)  $\beta$ -bromoethyl- $\alpha$ -chloromethyl ether are added dropwise at 50° C. The temperature is maintained at 50° C. for one hour. The formation of hydrochloric acid has then ceased. The reaction product is taken up in



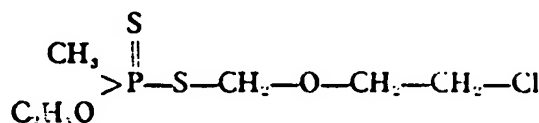
- 70 and of b.p. 98° C./0.01 mm Hg, are obtained. Yield 74% of the theoretical.

#### EXAMPLE 4.

- 75 126 grams (1 mol) dimethyl-thionothiophosphinic acid (m.p. 59° C.) are dissolved in 100 cc. benzene. 174 grams (1 mol)  $\beta$ -bromoethyl- $\alpha$ -chloromethyl ether are added at

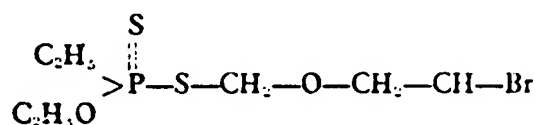


In the same way, the compound of the following formula may be obtained:



74 grams (0.25 mol) of the  $\beta$ -bromoethyl ester thus obtained are run at 20° C., with stirring, into a solution of 16 grams (0.25 mol) ethyl-mercaptan in 150 cc. benzene and a sodium ethylate solution containing 0.25 mol sodium. Stirring is continued at 20° C. for one hour and the reaction product then taken up in 200 cc. benzene and washed neutral with water. After drying with anhydrous sodium sulphate, it is fractionated. In this way 46 grams of the new ester:

300 cc. benzene, washed neutral with water and subsequently dried with anhydrous sodium sulphate. In this way, 170 grams  $\beta$ -bromoethyl ester of the formula:



and of b.p. 82° C./0.01 mm Hg are obtained. Yield 55% of the theoretical.

16 grams (0.25 mol) ethyl-mercaptan are dissolved in 150 cc. benzene, with the addition of a sodium ethylate solution containing 0.25 mol sodium. 77 grams (0.25 mol) of the above  $\beta$ -bromoethyl ester are added dropwise at 20° C., with stirring. Stirring is continued at 20° C. for one hour, the product then diluted with 200 cc. benzene, washed neutral with water and dried with anhydrous sodium sulphate. Upon fractionation, 53 grams of the new ester of the formula:

45° C. Stirring is continued at 50° C. for one hour. The formation of hydrochloric acid has now ceased. The reaction product is taken up in 300 cc. benzene, washed neutral with water and dried with anhydrous sodium sulphate. Upon distilling off the solvent, 198 grams  $\beta$ -bromoethyl ester of the formula: